CHEMICAL CHARACTERIZATION OF A hvb COAL

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Introduction

Numerous physical and chemical means are employed to elucidate the general properties and nature of coal (1,2,3). Coal has been examined directly as a solid and indirectly in liquefied form. Nevertheless, our present understanding of coal is surprisingly limited, preventing us from more efficient utilization of coal for energy and chemicals.

Ultimate and proximate analyses are routinely performed on coals, but most other information is general or descriptive. Direct examination of coal by various spectroscopic means have resulted in useful, but usually qualitative information. Solvent extraction has not been too successful due to poor solubility of coal in known solvents. Information from coal-derived liquids (CDL) has been related to the structure of coal only superficially. The complexity and insolubility of coal have defied many ingenious approaches and modern analytical means as far as the exact chemical nature of coal is concerned.

Here we report the development of a suitable scheme for characterizing CDL, which identified and quantified major structural units in a high volatile bituminous coal. We will describe how this characterization scheme for CDL was formulated, and discuss the preparation and characterization of three CDL's. Our findings will then be related to the chemical structure of the particular coal we examined.

Characterization Scheme for CDL

Since a complete analysis of CDL is impractical, if not impossible, due to the complexity in composition, "characterization" is performed, meaning determination of the quantitative distribution of compound types and the functional groups present. Although it is practical to do so, the nature of the characterization work needs to be carefully examined in terms of purpose, the material to be characterized, and the procedure.

The purpose of characterization in petroleum research has been mainly to obtain necessary information for further processing of petroleum or its fractions. In coal research, elucidation of the chemical structure of the CDL precursor (coal) is of much interest. Improvements in understanding of coal structure is essential in devising a better characterization scheme for CDL, which in turn will improve our understanding of coal structure.

Available information on coal and CDL (1-4) was carefully evaluated and incorporated into a new characterization scheme. Coal was considered as a composite of polymer-like materials. It may consist of numerous constituents having different types of structural units and linkages. Accordingly, the liquefaction of coal was assumed as basically a depolymerization process.

In preparing CDL, the following has been taken into consideration: (1) a CDL should represent the coal under investigation, (2) the degree of depolymerization needs to be carefully chosen, and (3) the liquids must be accessible by analytical means possibly at the molecular level. Based upon these considerations, CDL were prepared in high conversion processes (with a relatively high degree of depolymerization).

Considering the nature of the depolymerization process, the molecular size was chosen as a separation criterion for the fractionation of CDL, and vacuum distillation

was employed. For non-distillable CDL solvent extraction was used for separation. Each fraction from the separation was analyzed by elemental analysis, molecular weight determination and NMR spectroscopy. This scheme is different from others(5) previously employed, especially in the preparation of CDL and the methods used for the separations.

Experimental

A hvb coal (Clear Creek, Utah) was liquefied in a dry coiled-tube reactor(6). The coal had 39.1% of volatile matter, and its elemental composition (wt. percent) was: C, 76.1; H, 5.6; N, 1.4; and O, 17.9. Reaction conditions used in the liquefaction process were: T = 500°C; P_{H2} = 1800 psig; catalyst = 5% $ZnCl_2$; and residence time, several seconds. Product yields were: gases, 10%; light liquid, 5%; heavy liquid, 55%; char, 15%; and H_2O, 15% (based on MAF coal).

The heavy liquid had a boiling range from 250°C to more than 500°C, and accounted for more than 70% of the condensed-phase products which included light and heavy liquids, and char. The condensed-phase products were assumed to retain the skeletal structure of coal. This assumption was supported by C^{13} NMR analysis of starting coal and liquid products (7). Thus the heavy liquid was examined further in the subsequent investigation. Paraffinic material in the liquid was removed by solvent extraction. The liquid material remaining after this extraction was designated as HVL-P. HVL-P was distilled at temperatures below 260°C at a pressure of 3 Torr. The distillate was divided into three fractions, Light, Middle and Heavy according to their physical appearance with the non-distillable fraction termed Resid. Light and Middle were fluid at room temperature, but a phase separation appeared between them. Heavy and Resid were solids.

In another preparation of CDL's, the same coal was solubilized by reacting with sodium hydroxide and ethanol at 300°C and 320°C for 100 minutes in an autoclave using a procedure similar to that of Makabe (8). The products were named SP-300 and SP-320, the former being from 300°C runs and the latter being from 320°C runs. Each product was divided into four fractions. Two of them (Fractions I and J in SP 300, and Fractions I' and J' in SP-320) were soluble or floating in a strong basic solution, but precipitated in different fashion upon neutralization. The rest of the products were extracted with pyridine at room temperature to obtain Fractions K and K' (pyridine soluble) and pyridine insoluble portions.

Elemental composition was determined with a Perkin-Elmer Model 240 Analyzer. Oxygen was determined separately. NMR spectra were obtained with an EM-390 spectrometer (Varian). Pyridine-D_5 and $CDCl_3$ were used as solvent. Molecular weights were determined by vapor phase osmoemtry using a Corona Model 117 apparatus (Wescan Instruments, Inc.). The experimental procedure and conditions were carefully chosen to ensure the correct determination of molecular weight (9).

Results and Discussion

Structural parameters of average molecules in the CDL fractions were calculated from the elemental composition, molecular weight and proton NMR spectra. Their definitions and formulae (10) are:

Number of aromatic carbons

$$C_A = C - \frac{1}{2}(H_{2\alpha} + H_{\beta}) - \frac{1}{3}(H_{3\alpha} + H_{\gamma}) \quad (1)$$

Fraction of aromatic carbons (=aromaticity)

$$f_A = \frac{C_A}{C} \quad (2)$$

Total number of rings

$$R = \frac{2C - H + 2}{2} - \frac{1}{2} C_A \quad (3)$$

Number of aromatic clusters

$$C_{AP} = H_A + \frac{1}{2} H_{2\alpha} + \frac{1}{3} H_{3\alpha} \quad (4)$$

$$n = \#cl = \frac{1}{3} (C_{AP} - \frac{1}{2} C_A) \quad (5)$$

Number of aromatic rings

$$R_A = \frac{1}{4} (C_A - 2n) \quad (6)$$

Number of naphthenic rings

$$R_N = R - R_A \quad (7)$$

Values of C and H were from the empirical formula of each fraction. Hydrogen (H) was divided into four types based on NMR spectra: H_A, 5 - 9 ppm; $H_{2\alpha}$, 2.2 - 5 ppm: $H_{3\alpha}$, 2.0-2.2 ppm; H_β , 1.1-2.0 ppm; and H_γ, 0.3-1.1 ppm.

Table 1 summarizes yields from the distillation along with structural parameters of HVL-P fractions. All data are experimental values except for those in parentheses. Values in parentheses were calculated from those of the four fractions. The yields show that Light, Middle and Heavy fractions are a major portion of HVL-P.

Structural parameters change significantly from one fraction to another. For example, number of total rings, R, of HVL-P is 3.2, but it varies from 1.8 to 5.6 in its fractions. The number of total rings decreased by 1.9 from Resid to Heavy, 1.4 from Heavy to Middle, and 0.5 from Middle to Light. The number of aromatic rings, R_A, and molecular weight decreased in a similar fashion.

These differences are so large that the fractions were grouped into three, A, B, and C (Light and Middle, Heavy, and Resid respectively). The number of aromatic clusters (#Cl) reveals that most molecules in the first two groups (A and B) have one aromatic cluster, while about 30% of molecules in C have, on the average, two clusters. Overall, molecules in HVL-P have almost one aromatic cluster, indicating that HVL-P was essentially completely depolymerized.

Structural parameters were used to sketch possible structures of the four fractions. The structures in Fig. 1 contain the appropriate numbers of aromatic rings, aromatic clusters and naphthenic rings. The presence of functional groups or side chains on the structures are qualitative.

If one assumes that the aromatic double bonds were neither produced nor broken during the liquefaction process (in the production of HVL-P), the components in Group C were not converted to substantially smaller molecules (like A or B). Also Group B molecules were not converted to Group A. This non-convertibility indicates that the three groups were produced from three different structural units of the feed coal.

The assumption was drawn from the following consideration: (1) the liquefaction conditions were unfavorable for hydrogenation or dehydrogenation of aromatic structure in coal: most notably the residence time was too short, and (2) the large differences in molecular size among the three groups would have not resulted from the conversion of a large component group to a smaller one. Examination of the solubilization products, SP-300 and SP-320, provides further supporting information for this assumption as well as other interesting features of coal structure.

Table 2 contains yields and structural parameters of the solubilization products. As expected from the experimental conditions, the yields and molecular size of the products are substantially larger than those of HVL-P. Yet comparison of the structural parameters of HVL-P and SP-300 reveals a remarkable resemblance in an important structural feature: the average aromatic cluster sizes, R_A/#cl, are the same, 2.2, in both products. This agreement can be related to approximate size of the average aromatic cluster in coal.

Considering that 15% of the char yield and 5% of the light liquid yield in producing HVL-P, the average aromatic cluster size of the condensed-phase products (HVL-P, light liquid and char), which are supposed to retain the skeletal structure of coal, is expected to be larger than 2.2. On the other hand, SP-300 represents more than 97% of coal matrix (pyridine insoluble <2% of coal), but its average aromatic cluster size is supposed to have been reduced somewhat due to the nature of the reaction among coal, NaOH and ethanol. According to Makabe and Ouchi (8), the reaction slightly hydrogenates aromatic rings in coal under our experimental conditions. In any event, our observations on two separately prepared CDL's indicate that the size of the average aromatic cluster of the hvb coal is larger than 2.2, but not much different from 2.2.

The agreement in R_A/#cl between HVL-P and SP-300 suggest that large aromatic clusters like those (R_A/#cl = 3.4) in Resid of HVL-P should exist in SP-300, i.e. most probably in Fraction K. Comparison of the structural parameters of SP-300 with those of SP-320 helps clarify this point. The large difference in R_A/#cl between SP-300 and SP-320 is directly related to the question of the large aromatic clusters.

The difference in R_A/#cl is due to the conversion of Fraction K to a portion of Fraction J' and Fraction K' as revealed by their R_A/#cl's and yields. Fraction J' consists of two large portions, one coming from Fraction J and the other from Fraction K. Still Fractions J' and J behaved similarly in a strong basic solution as described in their preparation, and they have similar R_A/#cl and molecular weight (based on an estimation of a separate conversion of J to a portion of J'). This indicates that there was a portion of K which was similar to Fraction J in chemical structure, and which was different from the rest of K: the two portions are termed Fractions K_J and K_K respectively. Thus it is most likely that J and K_J experienced a similar transformation to become part of J'. In the conversion to J', apparently R_A/#cl of J was not changed, and so was not that of K_J. Then the large change of R_A/#cl between SP-300 and SP-320 is due to a large change of the same parameter between K_K and K'. R_A/#cl of K_K was large, but it reduced to that of K' upon the hydrogenation of NaOH/ethanol reaction.

Model compound studies by Ross and Blessing (11) support this interpretation. They observed that clusters consisting of single aromatic ring were not hydrogenated in a reaction with KOH/methanol at 400°C for 30 minutes, but a cluster containing three fused aromatic rings underwent hydrogenation. Estimation of R_A/#cl of K_K came out to be 3.4, which is the same as that of Resid in HVL-P. The large decrease in R_A/#cl, from 3.4 (for K_K) to 1.4 (for K') upon hydrogenation suggests that the aromatic rings in the clusters of K_K were mostly cata-condensed. Thus considerable amounts of polynuclear aromatic clusters were observed in HVL-P and SP-300 which were supposed to retain most of skeletal structure of the hvb coal.

Recently Whitehurst (12) and Farcasiu (13) reported that there is no significant amount of large aromatic clusters in coal. Their coals and experimental method were different from ours, but most notably their determination of the size of aromatic clusters was semi-quantitative (13). Although their conclusion might hold with the particular coals they examined, our findings support the conventional view that most bituminous coals contain considerable amounts of polynuclear aromatic clusters.

These observations lead to the conclusion that there were originally three classes of average aromatic clusters in terms of their size in the hvb coal. Two of them have, on the average, 1.9 and 1.3 aromatic rings per cluster, and they were collected in Fractions I' and J'. The third class has, on the average, 3.4 or more aromatic rings per cluster, and was collected in Fraction K mixed with the precursor of J'. The average size of the third class of clusters is expected to be larger than 3.4 since hydrogenation of the aromatic clusters is suspected as discussed previously. Now we will examine how these three classes of aromatic clusters would be further depolymerized.

The findings with SP-300 and SP-320 substantiate the assumption made earlier, i.e. that the aromatic double bonds experienced little change, if any, in the liquefaction

process in producing HVL-P. In the process, non-aromatic bonds between aromatic clusters in the coal were broken almost completely. Considering the milder reaction conditions in producing SP-300 and the same R_A/#cl of HVL-P and SP-300, further treatment of SP-300 in the liquefaction process would result in a complete depolymerization of SP-300 yielding a product similar to HVL-P. There are a couple of non-aromatic bonds linking aromatic clusters in SP-300 as revealed by #cl.

The comparison of structural parameters which are shown in Tables 1 and 2 provides detailed information on the conversion of SP-300 to completely depolymerized product. The three fractions of SP-300, however, were insufficiently depolymerized to draw useful information from their structural parameters. Instead the structural parameters of Fractions I' and J' were examined since Fractions I, J and K_J were converted to Fractions I' and J'. The numbers of aromatic rings, R_A's, of I' and J' are already smaller than that of Resid in HVL-P. Thus upon further depolymerization, Fractions I' and J' could become Light, Middle or Heavy such as those in HVL-P. According to R_A and #cl, 80% of J' will become Light or similar fraction in HVL-P (the predicted value is 17% of MAF coal, compared to 15% of Light plus light liquid). The rest of J' will become Heavy. Likewise, 70% of Fraction I' will become Middle/Heavy (the predicted value is 21%, compared to 17% of actual yield). The rest of I' will become Reside. Also the rest of SP-300, Fraction K_K, could become Resid/Char since both K_K and Resid have the same R_A/#cl (the predicted value came out to be the same as the actual yield, 35%). Taking account of the paraffinic material removed, 4%, and the loss, 5%, in preparing HVL-P, the predictions agree well with the actual yields.

The quantitative convertibility of SP-300 to HVL-P fractions further substantiates that the skeletal structures (or aromatic bonds) of coal were conserved during the liquefaction process as well as during the solubilization process at 300°C. Therefore the component groups A, B and C in HVL-P can be visualized as structural units of the coal. Almost all structural units were collected in SP-300 and they were grouped into three (Figure 2). The structural units in the first group, X, have one to two aromatic rings, and they are connected to each other by non-aromatic bonds. Although our data revealed that the linkages exist, their nature has not been studied yet. The structural units in the second group, Y, have two to three aromatic rings, and the third group consists of structural units having, on the average, four or more aromatic rings. Thus, the particular hvb coal has been characterized in terms of major structural units and their distribution. The same data analyzed so far provide valuable information also on the reduction of molecular size during the liquefaction, weak bonds, and the hydrogenation of aromatic clusters in coal, and this will be reported elsewhere.

Conclusion

A new characterization scheme for CDL has been devised based on the assumption that coal liquefaction is basically a depolymerization process. This scheme was instrumental in disclosing the following structural features of a hvb coal and its liquids:

(1) A CDL (HVL-P), produced at 500°C with very short residence time, was almost completely depolymerized, i.e., essentially all linkages between aromatic clusters were broken, and consisted of three major component groups, A, B and C. The components in Group A had mostly one aromatic ring, those in Group B two to three fused aromatic rings and those in Group C four or more fused aromatic rings. The fused aromatic rings have attachments such as naphthenic rings and aliphatic side chains. The three groups apparently are not convertible to each other under the liquefaction conditions used, and therefore, must have been produced from three different structural units in coal.

(2) A solubilization product (SP-300), obtained in a reaction with NaOH/ethanol at 300°C, revealed that it was less depolymerized than HVL-P, but the size of average aromatic cluster was the same, 2.2 aromatic rings per cluster, as that of HVL-P. SP-300 consisted of three classes of average aromatic clusters having 1.3, 1.9 and 3.4 aromatic rings per cluster. The distribution of the clusters was found by examining another solubilization product (SP-320)

prepared at 320°C. The aromatic rings of the large clusters appear to be cata-condensed.

(3) The clusters containing 1.3 and 1.9 aromatic rings per cluster are convertible to smaller species like Groups A and B in HVL-P, while the larger clusters of 3.4 aromatic rings will become Group C in HVL-P.

(4) The three groups of HVL-P were identified as the three major structural units of coal, and their distribution in the hvb coal was estimated from the examination of SP-300 and SP-320

These findings are unique to the characterization scheme for CDL. The results of this characterization of coal could be related to product potential in liquefaction, solvent refining and pyrolysis of coal. Taking into account the heterogeniety of coal and its inaccessibility by analytical means, the present approach appears to be a practical, useful way to characterize the chemical structure of coal. The same approach will be utilized with other coals which can be solubilized to further substantiate this method.

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References

(1) Lowry, H.H., Ed. Chemistry of coal Utilization, Supp. Vol., John Wiley and Sons, New York, 1963.

(2) Van Krevelen, D.W., Coal, Elsevier Publishing Co., New York, 1961.

(3) Friedel, R.A., Ed. Spectrometry of Fuels, Plenum Press, New York, 1970.

(4) Larsen, J.W., Ed. Organic Chemistry of Coal, ACS Symposium Series 71, Am. Chem. Soc., Washington, D.C., 1978; Vahrman, M. Chem. Bit. 8, 16, 1972.; McIntosh, M.J., Fuel 55, 59, 1976.; Wiser, W.H., Anderson, L.L., Qader, S.A., and Hill, G.R., J. Appl. Chem. Biotech. 21, 82, 1971.; Gould, R.F., Ed. Coal Science, Adv. in Chem. Series 55, Am. Chem. Soc., 1966.; Neavel, R.C., Preprints, Div. of Fuel Chem., Am. Chem. Soc., 24 (1) 73, 1979.

(5) Farcasiu, M., Fuel, 56 9, 1977.; Given, P.H., Cronauer, D.C., Spakman, W., Lovell, H.L., Davis, A., and Biswas, B. Fuel, 54, 40, 1975.; Schultz, H. and Mima, M.J., Preprints, Div. of Fuel Chem., Am. Chem. Soc., 23 (2) 76, 1978.

(6) Wood, R.E., and Wiser, W.H., Ind. Eng. Chem., Process Res. Devel., 15, 144, 1976.

(7) Zilm, K.W., Pugmire, R.J., Grant, D. M., Wood, R.E., and Wiser, W.H., Fuel, 58, 11, 1979.

(8) Makabe, M., and Ouchi, K. Fuel Proc. Tech., 2 131, (1979).

(9) Chung, K.E., Anderson, L.L., and Wiser, W.H., Fuel, accepted for publication.

(10) Chapter XXII in Reference (2).; Clutter, D.R., Petrakis, L., Stenger, R.L., Jr., and Jensen, R.K., Anal. Chem. 44 (8) 1395, 1972.; Kanda, N., Itoh, H., Yokoyama, S., and Ouchi, K., Fuel, 57, 677, 1978.

(11) Ross, D.S., and Blessing, J.E. Preprints, Div. of Fuel Chem., Am. Chem. Soc., 24 (2), 125 (1979).

(12) Whitefurst D.D., Organic Chemistry of Coal, Ed. by Larson, J.W., ACS Symposium Series 71, Am. Chem. Soc., Washington, D.C. 1978, p. 1.

(13) Farcasiu, M., Preprints, Div. Fuel Chem., Am. Chem. Soc., 24 (1) 121, 1979.

TABLE 1

Analytical Data on HVL-P and Its Fractions

	Yield, Wt%	Mol. Wt.	R_A	R_N	#cl	f_a
HVL-P	100 (92.5)*	258 (268)	2.4 (2.4)	0.8 (0.9)	1.1 (1.1)	0.63 (0.60)
Light	19.2	183	1.2	0.6	1.0	0.55
Middle	15.7	210	1.6	0.7	1.1	0.58
Heavy	17.6	272	2.4	1.3	1.0	0.59
Resid	40.0	396	4.4	1.2	1.3	0.68

*Calculated from those of the four fractions.

TABLE 2

Structural Parameters of the Solubilization Products

	Yield*	Mol. Wt.	R_A	R_N	#cl	f_A	R_A/#cl
SP-300**	85.7	843	5.6	3.9	2.6	0.52	2.2
Fraction I	23.9	777	5.0	3.3	2.7	0.52	1.9
J	9.1	643	3.4	3.4	2.5	0.53	1.4
K	52.7	930	6.6	4.4	2.6	0.51	2.5
SP-320**	76.5	520	3.2	2.4	2.1	0.52	1.5
Fraction I'	26.6	478	3.2	2.3	1.7	0.55	1.9
J'	23.8	444	2.4	2.0	1.8	0.50	1.3
K'	26.1	690	4.4	3.1	3.1	0.52	1.4

*Weight % of coal (MAF)

**The parameters were calculated from the three fractions.

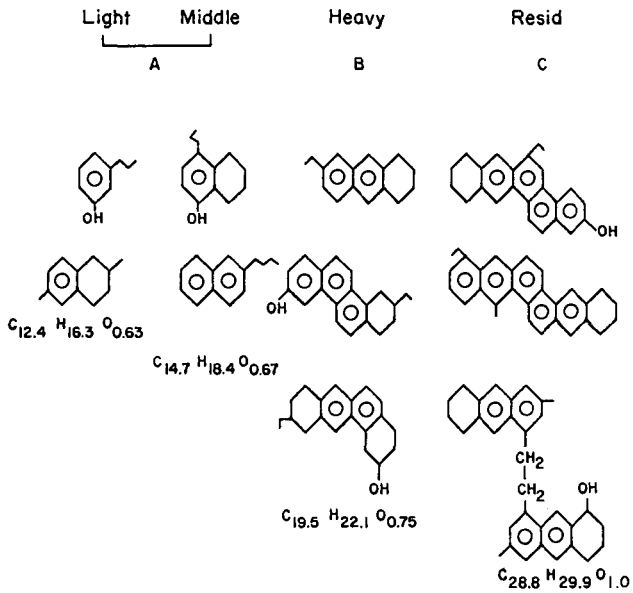

Figure 1. Sketches of Possible Structures of HVL-P Fractions.

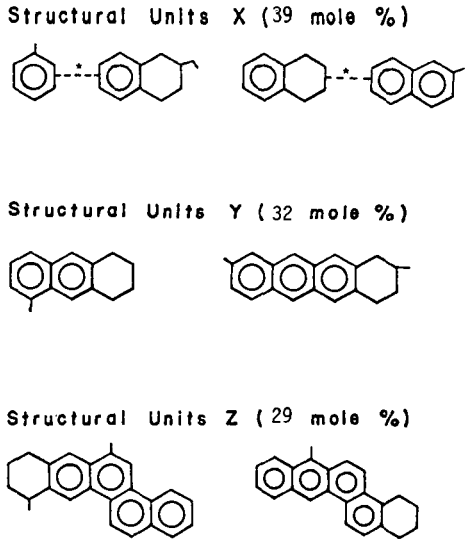

Figure 2. Structural Units Comprising A hvb Coal

*Linkages exist but were not identified.